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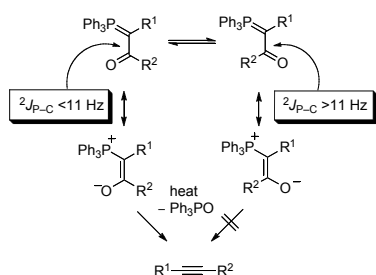
The Value of $^2J_{\text{P-C}}$ as a Diagnostic Parameter for the Structure and Thermal Reactivity of Carbonyl-Stabilised Phosphonium Ylides

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The value of $^2J_{\text{P-CO}}$ as a diagnostic parameter for the structure and thermal reactivity of carbonyl-stabilised phosphonium ylides

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ABSTRACT

A survey of 20 carbonyl-stabilised phosphonium ylides with recently reported X-ray structures shows a strong correlation between the C=P to C=O torsion angle and the value of $^2J_{\text{P-CO}}$, with high values being associated with an *anti* configuration and low with *syn*. Seven new X-ray structural determinations are reported, several for types of ylide not crystallographically characterised before, and these also conform to this pattern. The value of $^2J_{\text{P-CO}}$ is then correlated with whether or not thermal extrusion of Ph_3PO occurs to give alkynes for over 200 ylides and an empirical rule developed that the extrusion never occurs for ylides where this value is >11 Hz. This is used to rationalise the anomalous behaviour of some trioxo ylides and cyclic ylides, two of which afford cycloalkynes, isolated after rearrangement as the isomeric 1,3-dienes. The rule also holds for a family of novel highly fluorinated ylides which afford fluorinated alkynes in good yield upon flash vacuum pyrolysis.

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1. Introduction

Phosphonium ylides stabilised by the presence of one or more adjacent carbonyl functions continue to be of interest, both as synthetic intermediates in organic chemistry,^{1–5} and as ligands for transition metals.^{6–8} Fundamental to both these applications is the significant contribution to their structures from phosphonium enolate forms **3** and **4** which mean that the compounds can exist as *Z* and *E*-isomers **1** and **2** with a significant barrier to interconversion (Figure 1). This phenomenon was observed by ^1H NMR spectroscopy at an early date,^{9–14} and has more recently been investigated, particularly for ylides with two stabilising groups, by a combination of IR spectroscopy, theoretical methods and X-ray crystallography by Castañeda and co-workers.^{15–17} In some of these studies NMR chemical shifts have also been examined and previous studies have described trends in ^{31}P NMR chemical shifts,¹⁸ ^{13}C NMR chemical shifts and $^1J_{\text{C-P}}$ for the ylide carbon,¹⁹ and even ^{17}O NMR chemical shifts.²⁰ In this paper we show for the first time that the value of the two-bond coupling constant, $^2J_{\text{P-CO}}$, readily observed in the ^{13}C NMR spectra of such compounds, is a diagnostic parameter for the relative importance of *Z* and *E* forms. Although this parameter does not seem to have been systematically studied before, we have found it to be a reliable indicator not only of the structural situation in a given ylide but also of the likelihood of thermal elimination of Ph_3PO being possible. In previous work,²¹ we found that some trioxoylides did eliminate Ph_3PO thermally to give diacyl alkynes

while others did not, and the behaviour seemed to correlate with the value of $^2J_{\text{P-CO}}$, but X-ray structural evidence was lacking. We now describe a total of seven new X-ray structure determinations of carbonyl-stabilised ylides, as well as a much wider correlation between the value of $^2J_{\text{P-CO}}$ and both their solid-state structure and reactivity towards thermal fragmentation.

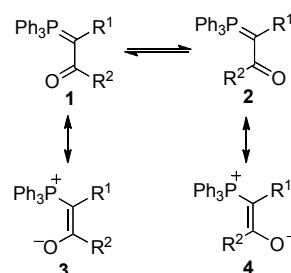


Figure 1. Contributing resonance forms for carbonyl-stabilised ylides

2. Results and Discussion

Some time ago we surveyed all X-ray structures of carbonyl-stabilised ylides published up to that time,²² and established some clear trends, namely that keto carbonyls were generally *syn* to the ylide function (i.e. as in **1** or **3**) while ester carbonyls were generally *anti* (as in **2** or **4**), a pattern later confirmed by other

workers.⁷ To place our new results in context, Table 1 summarises the key geometric parameter for recently reported mono- and dicarbonyl ylides as well as the values of $^2J_{\text{P-CO}}$ where these are known. In the case of **24** no coupling constant was reported,²³ presumably due to line broadening resulting from restricted rotation at RT, but we were able to measure the value by recording the spectrum at 55°C.

Table 1: Torsion angles and $^2J_{\text{P-CO}}$ for ylides with recently reported X-ray structures

Cmpd	R ¹	R ²	CCDC Ref. Code	P=C-C=O Torsion (°)	Ref	$^2J_{\text{P-C=O}}$ (Hz)	Ref
5	H	Ph	HEVKIC	2.2 / 0.9	24	3.0	25
6	H	2-Thienyl	QIXQIY	9.7	26	3.7	27
7	H	4-BrC ₆ H ₄	UDURAN	2.8	28	3.3	29
8	CN	Me	WEVXIF	3.3	30	3.7	31
9	CN	OMe	WEVXEB	4.4	30	—	
10	H	4,4'-bi-phenylene	FUWGIO	7.0	32	<2	32
11	—	—	AWIKUN	177.3	33	—	
12	OMe	Me	GUKTUB	162.4 (R ¹) 12.0 (R ²)	34	15.3 (R ¹) 3.3 (R ²)	15
13	OEt	Me	VAVWEU 01	170.8 (R ¹) 1.8 (R ²)	34	15.0 (R ¹) 4.1 (R ²)	15
14	OPr ⁱ	Me	GUKVEN	174.8 (R ¹) 1.0 (R ²)	34	15.3 (R ¹) 3.3 (R ²)	15
15	OBu ^t	Me	GUKVIR	159.5 (R ¹) 2.7 (R ²)	34	14.3 (R ¹) 3.8 (R ²)	15
16	OEt	CH ₂ CO ₂ Et	AWIKIB	169.4 (R ¹) 3.5 (R ²)	33	15.5 (R ¹) 5.2 (R ²)	35
17	OEt	OMe	LICLIT	154.2 (R ¹) 10.2 (R ²)	36	12.8 (R ¹) 12.7 (R ²)	37
18	OPr ⁱ	OMe	PODSOR	167.6 (R ¹) 16.9 (R ²)	38	11.0 (R ¹) 12.8 (R ²)	39
19	OPr ⁱ	OEt	PODSUX	170.4 (R ¹) 6.7 (R ²)	38	12.5 (R ¹) 13.5 (R ²)	39
20	OBu ^t	OMe	PODTAE	179.5 (R ¹) 9.6 (R ²)	38	10.4 (R ¹) 15.2 (R ²)	39
21	OBu ^t	OEt	PODTEI	162.5 (R ¹) 4.2 (R ²)	38	12.8 (R ¹) 14.6 (R ²)	39
22	Me	Me	SASZOC	164.6 18.2	40	7.9	23
23	OMe	OMe	LICLOZ	158.2 / 154.6 162.0 / 8.8	36	13.5	37
24	OEt	OEt	SASZUI	170.7 149.8	40	13.1	this work

Among the keto ylides **5–8** and **10** (Figure 2) the carbonyl group is oriented *syn* to phosphorus as expected.²² For **9** the *syn* orientation might seem surprising but several other simple ylides

with a *syn* ester carbonyl are known.²² The *anti* arrangement of the ester carbonyl as in **11** is more usual.

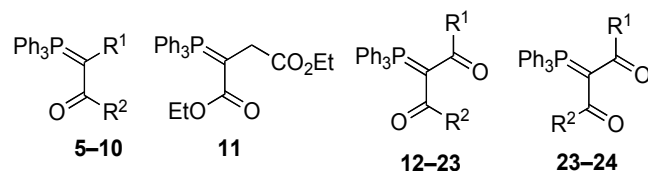


Figure 2. Structure of compounds referred to in Table 1

The pattern among the remaining compounds **12–24** is more interesting. For **12–16** where there are both ketone and ester carbonyls, they are respectively oriented *syn* and *anti* to P as expected, and in agreement with the previously published structure in the case of **13**.⁴¹ The ylides **17–21** with two different ester groups follow a consistent pattern with the carbonyl of the more bulky ester group aligned *anti* to P and the less bulky *syn* to it. The remaining symmetrical compounds **22–24** have one carbonyl *syn* and one *anti* for **22**, both carbonyls *anti* for **24**, and for **23** there are two different molecules, one of each type, in the unit cell. If we now examine the reported values of $^2J_{\text{P-CO}}$ for these compounds (Table 1), a clear pattern is evident, with ketone carbonyls showing a value between 3 and 8 Hz while ester carbonyls have a higher value between 10 and 16 Hz. It should be noted that it has been possible to unambiguously assign the different carbonyls in compounds **17–21** since the authors also reported non H-decoupled ¹³C spectra. Particularly from the latter cases, it is evident that the magnitude of $^2J_{\text{P-CO}}$ correlates to the nature (ketone vs. ester) of the carbonyl function and not to its alignment in solid state or solution. However as will be discussed later, for most carbonyl ylides the value of $^2J_{\text{P-CO}}$ does act as a reliable predictor of the pyrolysis behaviour.

We have now determined the X-ray structures of the mono- and dicarbonyl ylides **25**, **26**, **27**, **30** and **31**. It seems anomalous that the structure of the simple acetyl ylide **25** has not previously been reported. The pivaloyl ylide **26** is the first to be structurally characterised which is derived from a phosphine with three different groups and, since the phosphine involved is readily available in enantiomerically pure form by kinetic resolution,^{42,43} this paves the way for formation of *P*-chiral ylides.

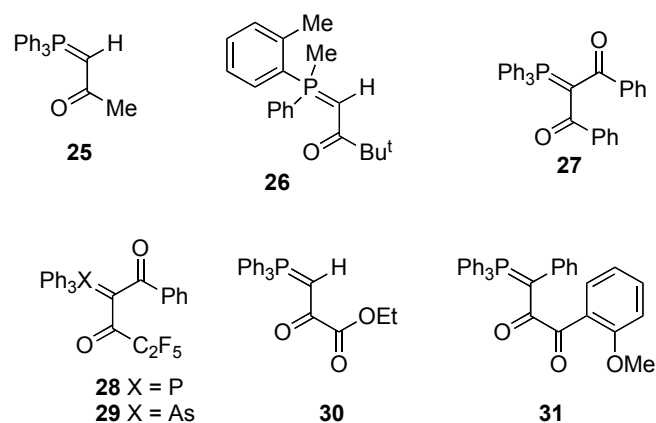


Figure 3. Mono- and dicarbonyl ylides studied crystallographically with comparison compounds

The structure of **25** is shown in Figure 4. As expected it has a *syn* arrangement of C=O and C=P and the bond lengths are typical for a ketone-stabilised ylide, consistent with its low value of $^2J_{\text{P-CO}}$ of 2.4 Hz.²⁵ The more complex ylide **26** was formed

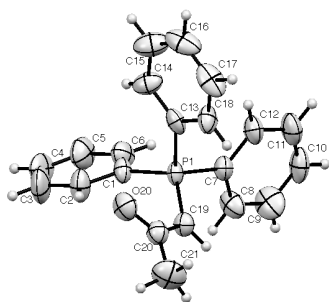


Figure 4. X-Ray structure of the oxo ylide **25** (ORTEP diagram, 50% level). Selected bond lengths and torsion angles; P(1)–C(19) 1.716(7), C(19)–C(20) 1.387(10), C(20)–O(20) 1.249(9) Å; P(1)–C(19)–C(20)–O(20) 5.5(10)°

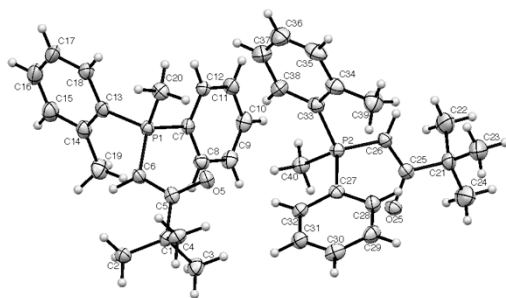


Figure 5. X-Ray structure of the oxo ylide **26** (ORTEP diagram, 50% level). Selected bond lengths and torsion angles; P(1)–C(6) 1.723(3), C(6)–C(5) 1.404(5), C(5)–O(5) 1.261(4), P(2)–C(26) 1.714(3), C(25)–C(26) 1.393(5), C(25)–O(25) 1.261(4) Å; P(1)–C(6)–C(5)–O(5) –2.1(4), P(2)–C(26)–C(25)–O(25) –3.5(4)°

from the racemic tertiary phosphine⁴² by reaction with bromopinacolone followed by treatment with aqueous NaOH in good yield.⁴⁴ Its structure (Figure 5) consists of two slightly different molecules in the unit cell but they both show bond lengths typical of a ketone-stabilised ylide and have a *syn* arrangement of C=O and C=P. The value of $^2J_{\text{P-CO}}$ was found to be <2 Hz.⁴⁴

We have also determined the structure of the dibenzoyl ylide **27**. The published synthesis for this,⁴⁵ involving treatment of the monobenzoyl ylide with a large excess of benzoic anhydride in chloroform and subsequent separation of the product from unreacted benzoic anhydride and benzoic acid, was found to be unsatisfactory so an improved method was developed for which full details are given in the Experimental Section. The supposed reason for using the anhydride rather than the more normal benzoyl chloride⁴⁶ was to avoid *O*-acylation, but a later report⁴⁷ that heating the initially formed *O*-benzoyl salt led to rearrangement to the *C*-benzoyl isomer made it clear that these are, respectively, kinetic and thermodynamic products. With this in mind, we confirmed that treatment of the monobenzoyl ylide with one equiv. each of benzoyl chloride and triethylamine gave **27** in 71% yield after recrystallisation. The structure (Figure 6) showed both carbonyls to be roughly *syn* to C=P in marked contrast to the diacetyl ylide **22**, which appears to be the only other structurally characterised symmetrical diketone stabilised ylide. The torsion angles for **27** at 28.6° and 13.2° are rather large however, and somewhat reminiscent of the situation for the unsymmetrical diketo ylides of phosphorus and arsenic, **28**⁴⁸ and **29**⁴⁹ which have torsion angles of 65.2° (COPh) and 5.3°

(COCF₂CF₃), and 34.4/37.7° (COPh) and 7.1/7.8° (COCF₂CF₃), respectively (**29** has two forms in the unit cell). It seems that the large size of Ph broadly favours the *syn* as opposed to *anti* arrangement but, with two equivalent benzoyl groups present, the energy to be gained by a strictly *syn* arrangement is not sufficient to overcome the effects of crystal packing forces which result in a somewhat distorted structure. The value of $^2J_{\text{P-CO}}$ for this compound is discussed later as we have recorded its ¹³C NMR spectrum for the first time.

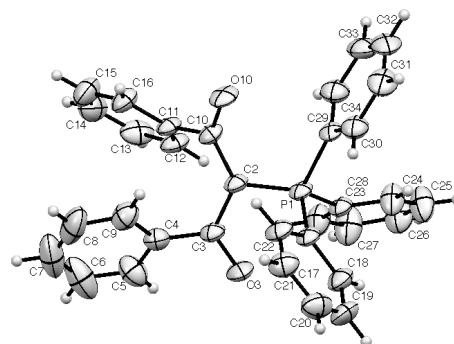


Figure 6. X-Ray structure of the dioxo ylide **27** (ORTEP diagram, 50% level). Selected bond lengths and torsion angles; P(1)–C(2) 1.757(3), C(2)–C(3) 1.443(5), C(3)–O(3) 1.258(4), C(3)–C(4) 1.472(5), C(2)–C(10) 1.450(5), C(10)–O(10) 1.245(4), C(10)–C(11) 1.501(5) Å; P(1)–C(2)–C(10)–O(10) –28.6(5), P(1)–C(2)–C(3)–O(3) –13.2(4)°

One type of ylide for which there appear to be no previous X-ray structures are those with a 1,2-dicarbonyl function on one side and no carbonyls on the other. In these the torsion angles between the two carbonyl groups as well as between C=O and C=P are of interest as described for higher polyoxo ylides in our previous work.²² Two examples of this type are now reported, **30** with an ester function (Figure 7), and **31** with a ketone function (Figure 8).

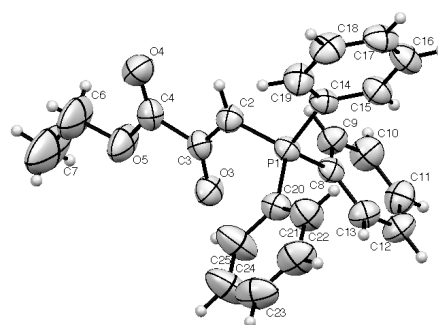


Figure 7. X-Ray structure of the dioxo ylide **30** (ORTEP diagram, 50% level). Selected bond lengths and torsion angles; P(1)–C(2) 1.725(2), C(2)–C(3) 1.380(3), C(3)–O(3) 1.250(2), C(3)–C(4) 1.534(3), C(4)–O(4) 1.195(2), C(4)–O(5) 1.313(3) Å; P(1)–C(2)–C(3)–O(3) 1.5(3), O(3)–C(3)–C(4)–O(4) –176.5(2)°

Both these show a similar pattern: the first C=P *syn* to P=C (torsion angle 1.5° for **30** and 5.8° for **31**) and the second C=O either *anti* to the first (torsion angle 176.5°) for **30** or at an intermediate angle (torsion angle 113.8°) for **31**.

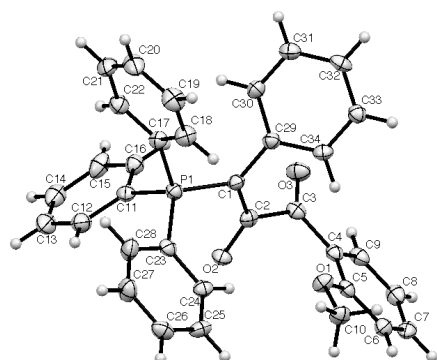


Figure 8. X-Ray structure of the dioxo ylide **31**. Selected bond lengths and torsion angles; P(1)–C(1) 1.751(3), C(1)–C(2) 1.392(4), C(2)–O(2) 1.263(4), C(2)–C(3) 1.536(4), C(3)–O(3) 1.227(3) Å; P(1)–C(1)–C(2)–O(2) –5.8(4), O(2)–C(2)–C(3)–O(3) 113.8 (3)°.

Finally we have determined the X-ray structure of the trioxo ylide **32** (Figure 9), one of the anomalous trioxo ylides in our previous study²¹ that did not eliminate Ph_3PO across the central position to give a diacyl alkyne but rather decomposed to give no useful products. The *syn* relationship between P=C and the "outer" C=O (torsion angle 20.1°) coupled with the *anti* relationship with the "central" C=O (torsion angle 177.4°) is consistent with the failure of the pyrolysis to produce a diacyl alkyne.²¹ The values of $^2J_{\text{P-C=O}}$ (6 Hz to COMe but 13 Hz to CO-CO₂Me) suggest that this is also the predominant configuration in solution. We believe that, in this and the other cases where pyrolysis fails, Ph_3PO is eliminated between the ylide and the *syn* carbonyl to give the alkynyl-1,2-dicarbonyl product which is unstable. There are only very few reports of compounds containing a $-\text{C}\equiv\text{C}-\text{CO}-\text{CO}-$ function in the literature,⁵⁰ and the product expected from **32** $\text{MeC}\equiv\text{C}-\text{CO}-\text{CO}_2\text{Me}$ is apparently too unstable to survive the conditions of the pyrolysis and decomposes.

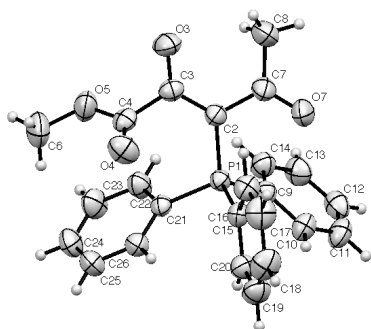


Figure 9. X-Ray structure of the trioxo ylide **32**. Selected bond lengths and torsion angles; P(1)–C(2) 1.760(2), C(2)–C(7) 1.462(3), C(7)–O(7) 1.226(2), C(2)–C(3) 1.421(3), C(3)–O(3) 1.239(2), C(3)–C(4) 1.523(3), C(4)–O(4) 1.196(2) Å; P(1)–C(2)–C(7)–O(7) –20.1(2), P(1)–C(2)–C(3)–O(3) 177.4(2), O(3)–C(3)–C(4)–O(4) –111.9(2)°.

The link between the solid state configuration as determined by X-ray diffraction and the P–C coupling constants observed in solution phase NMR is shown in Figure 10 for the "badly-behaved" ylide **32** as compared to a typical trioxo ylide **33** which does eliminate Ph_3PO efficiently to give $\text{PhCO}-\text{C}\equiv\text{C}-\text{COMe}$.^{21,22} It is interesting to note a similar relationship also for the

iminodioxo ylide **34** which decomposes under FVP conditions to regenerate $\text{Ph}_3\text{P}=\text{NPh}$ and DMAD, the components from which it was made.⁸

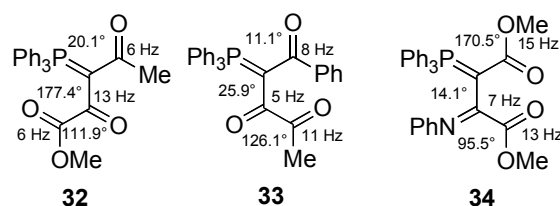


Figure 10. Torsion angles and P–C coupling constants for polyoxo ylides.

Since the pattern of P–CO coupling constants seems to have some diagnostic value in predicting the likely success of thermal Ph_3PO elimination, we have conducted a wider survey of this phenomenon and present in Table 2 data for a large number of ylides and groups of ylides for which both the coupling constants and pyrolysis behaviour is known. These are given in descending order of $J_{\text{P-CO}}$.

Table 2: Value of $^2J_{\text{P-CO}}$ and pyrolysis behaviour for carbonyl-stabilised ylides **1**

Cmpd	R ¹	R ²	$^2J_{\text{P-C=O}}$ (Hz)	Ref	Pyrol. to Ph_3PO and $\text{C}\equiv\text{C}$?	Ref
24	Me	H	26.0	^a	NO	51
	CO ₂ Et	OEt	13.1	^a	NO	^a
	H	OMe	12.7	⁵²	NO	^a
35	H	OEt	12.1	⁵²	NO	^a
	—	—	11.3	^a	NO	^a
	Ph	C≡CPh	10.9	⁵³	YES	53
	CO ₂ Et	C≡C–C≡CAr	9.8	⁵⁴	YES (1 example)	54
	R	C≡CR	9–11	⁵³	YES (7 examples)	53
40	COCOR	CO ₂ R	9.0	⁵⁵	YES (3 examples)	55
	CO ₂ Et	C≡CPr ⁿ	8.6	⁵⁴	YES	54
	C ₆ F ₅	CF ₃	8.2	^a	YES	56
	CO ₂ Et	C≡CAr	8–9	⁵⁴	YES (11 examples)	54
	C ₆ F ₅	C ₆ F ₅	8.0	^a	YES	57
22	COMe	Me	7.9	²³	YES	45
31	Ph	COCOAr	7.0	⁵⁸	YES	58
38	4-CF ₃ C ₆ F	CF ₃	7.0	^a	YES	^a
27	COPh	Ph	7.0	^a	YES	45
44	4-CF ₃ C ₆ F	CO ₂ Me	6.8	^a	YES	^a
45	4-CF ₃ C ₆ F	CO ₂ Et	6.6	^a	YES	^a
39	4-CF ₃ C ₆ F	C ₆ F ₅	6.6	^a	YES	^a
43	CO ₂ Me	CF ₃	6.1	^a	YES	59
42	2-MeN	CH=CHAr	6.0	⁴	YES (3 examples)	⁴
	BnC ₆ H ₄					
	CN	C ₆ F ₅	5.8	^a	YES	^a
	CO ₂ Et	CF ₃	5.8	⁶⁰	YES	60
	CO ₂ Me	Ar	5.2–6	⁶¹	YES (4 examples)	61

	Ph	CH=CHPh	5.4	⁶²	YES	⁶²
15	CO ₂ Et	CH ₂ CO ₂ Et	5.2	³⁵	YES	³⁵
	COR ¹	(CH ₂) ₂ COR ²	5–6	⁶³	YES (6 examples)	⁶³
	Ph	arenediyl	5–6	⁶⁴	YES (2 examples)	⁶⁴
	CO ₂ Et	arenediyl	5–6	⁶⁴	YES (6 examples)	⁶⁴
	Ph	Ph	5.0	⁶⁵	YES	⁵¹
	alkyl/Ar	CH=CHAr	5.0	^{62,66}	YES (29 examples)	^{62,66-7}
30	H	CO ₂ Et	5.0	⁵⁵	YES	⁵⁵
	2-MeS-3-pyridyl	CH=CHAr	5.0	⁵	YES (4 examples)	⁵
	CO ₂ Bu ^t	CH ₂ R	4.3	⁶⁸	—	
37	—	—	4.2	^a	YES	^a
	CO ₂ R	COR or CO ₂ R	4–6	²¹	YES (8 examples)	²¹
	CO ₂ Et	(CH ₂) ₂ CO ₂ CHPh	3.7	⁶⁹	—	
36	—	—	3.7	^a	YES	^a
	CO ₂ Me	alkyl or Ar	3.3	¹⁵	YES (11 examples)	⁷⁰
25	H	Me	2.4	²⁵	YES	⁷¹
	CO ₂ Et	alkyl or Ar	2–7	⁷²	YES (18 examples)	^{72,73}
	R	2-MeO/MeSC ₆ H	2–7	^a	YES (12 examples)	⁷⁴
	o-Anis	R	2–6	⁷⁵	YES (6 examples)	⁷⁵
26	—	—	<2	⁴⁴	YES	^a
	H	Ph	<2	⁷⁶	YES	⁷¹
	H	alkyl	<2	^a	YES (7 examples)	⁷¹
	alkyl	alkyl	<2	^a	YES (8 examples)	⁷¹
	H	CO ₂ Me	<2	⁵⁵	YES	⁵⁵
	CO ₂ Et	CH(R ¹)NHCO ₂ R	<2	³	YES (12 examples)	³

^a This work

The highest value observed is for the formyl ylide, which was noted in the earliest studies not to undergo alkyne formation upon pyrolysis. This is readily understandable given the *anti* configuration indicated by the high value. There is an erroneous literature report⁷⁷ listing the carbonyl doublet in the ¹³C NMR spectrum for this compound as two singlets. The failure of simple alkoxy carbonyl ylides to eliminate Ph₃PO thermally to afford alkoxy alkynes is also well documented and consistent with their high *J* values. As can be seen from the remainder of the Table, the majority of ylides listed do undergo thermal alkyne formation by extrusion of Ph₃PO and the values of ²*J*_{P-CO} range from 9–10 Hz right down to <2 Hz. There appears to be a cut-off value around 11 Hz above which extrusion does not occur.

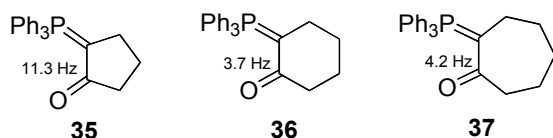
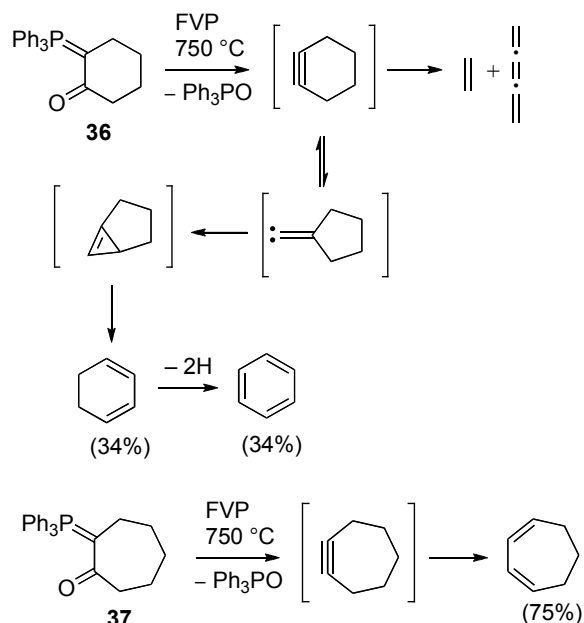


Figure 11. Structures of the cyclic ylides **35–37** with values of ²*J*_{P-CO}.

An interesting test of this theory is provided by the series of three cyclic oxo ylides **35–37** (Figure 11) which are rigidly held in a *syn* configuration. These are of particular interest since elimination of Ph₃PO would give the corresponding

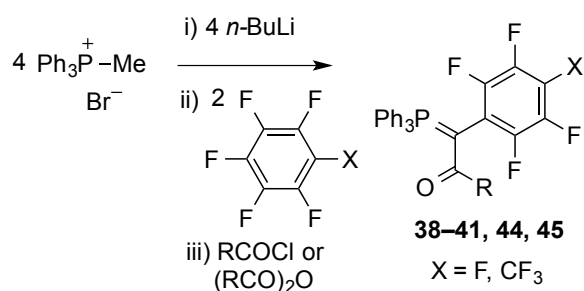
cycloalkynes: cyclopentyne, cyclohexyne and cycloheptyne. These reactive intermediates were first generated by Wittig over 50 years ago⁷⁸ but there has recently been renewed interest in their generation⁷⁹ and the use of cyclohexyne in synthesis.⁸⁰ Although these ylides have not been examined as a source of cycloalkynes before, there is a single brief report of 2-tributylphosphoranylidene cyclopentane-1,3-dione and the corresponding cyclohexanedione being treated with Me₃SiCl to generate, respectively, cyclopentyne and cyclohexynone which were trapped by cycloaddition.⁸¹ The three compounds **35–37** were prepared using the published method⁸² and, as shown in Figure 11 and Table 2, the five-membered ring ylide **35** has a very high coupling constant. In agreement with this, it was recovered largely unchanged from FVP at temperatures up to 850 °C and when higher temperatures were used there was complete decomposition with only low yields of benzene and triphenylphosphine identified among the products. In contrast, the six- and seven-membered ring ylides **36** and **37** with lower values of ²*J*_{P-CO} reacted cleanly at 750 °C to give a high yield of Ph₃PO together with 1,3-cyclohexadiene (34%) and benzene (34%) from **36** and 1,3-cycloheptadiene (75%) from **37** (Scheme 1).



Scheme 1. Thermal decomposition of **36** and **37** using FVP

These are the same products formed in previous attempts to generate cyclohexyne and cycloheptyne under FVP conditions, for example from the corresponding cycloalkylidene Meldrum's acid derivatives.⁸³ Although later evidence⁸⁴ suggested that the first reaction actually proceeds mainly via ketenes directly to the cyclopentylidenecarbene, thus bypassing cyclohexyne, the detection of butatriene⁸⁵ showed that cyclohexyne must be involved to some extent. Here in contrast, we are approaching the well known⁸⁶ cycloalkyne to cycloalkylidenecarbene rearrangement from the opposite direction, since it seems inconceivable that **36** could lose Ph₃PO to give cyclopentylidenecarbene directly without going through cyclohexyne. In addition a low (ca. 2%) yield of butatriene was also formed from **36** under our conditions as shown by the appearance of characteristic ¹³C NMR signals at δ_C 170.9 and 95.7. The formation of 1,3-cycloheptadiene from **37** is proposed to proceed by the corresponding route with ring-contraction of cycloheptyne giving cyclohexylidenecarbene which undergoes intramolecular CH insertion followed by rearrangement.⁸³

We have also examined a series of stabilised ylides bearing perfluorinated groups and report here the ^{13}C NMR data and pyrolysis behaviour for compounds **38–45** as well as an X-ray structure for **38**. As noted by previous workers,^{56, 57, 59} this provides a useful synthetic approach to perfluorinated alkynes but the value of $^2J_{\text{P-CO}}$ has not so far been reported for any such ylides. Conventional synthetic approaches⁵⁷ to ylides of this type are limited by the high cost of perfluorinated benzyl halides. However we were able to use a modified procedure first described by Shen and Qiu⁵⁶ in which methylenetriphenylphosphorane reacts with hexafluorobenzene with displacement of one fluorine atom, followed by an acylating agent, to give the target ylides **40** and **41** (Scheme 2). Applying this method to perfluorotoluene led to regiospecific displacement of the *para* fluorine to give the new ylides **38**, **39**, **44** and **45**. The stabilised ylides **42** and **43** were prepared using acylation of the methoxycarbonyl- and cyanomethylene ylides in the presence of triethylamine.⁵⁹



Scheme 2. Synthesis of perfluorinated ylides

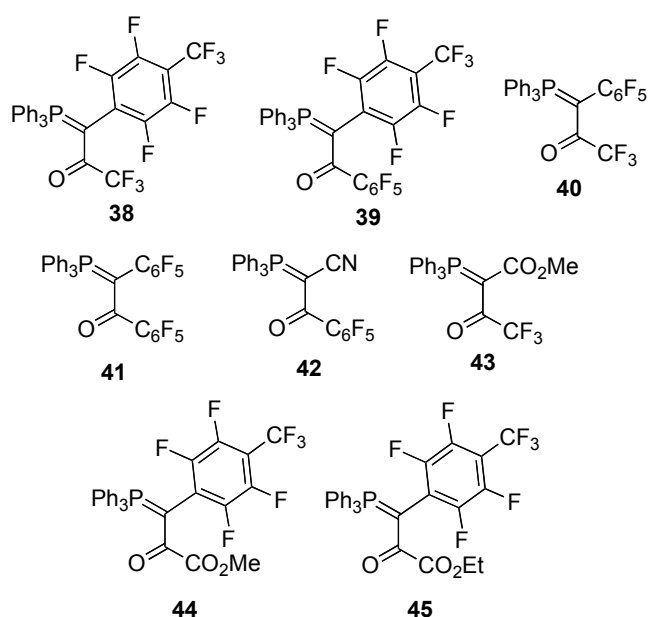


Figure 12. Fluorinated ylides prepared

The eight fluorinated ylides prepared are shown in Figure 12, and as listed in Table 2, they all show values of $^2J_{\text{P-CO}}$ in the range 5.8–8.2 Hz suggesting the likely success of thermal elimination of Ph_3PO .

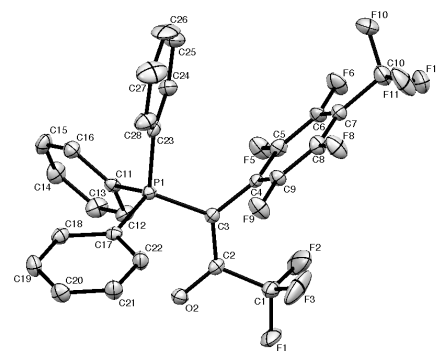


Figure 13. X-Ray structure of fluorinated oxo ylide **38**. Selected bond lengths and torsion angles; P(1)–C(3) 1.757(4), C(3)–C(2) 1.385(5), C(2)–O(2) 1.255(4) Å; P(1)–C(3)–C(2)–O(2) +2.9(5)°.

The ylide **38** formed crystals suitable for X-ray diffraction and the structure (Figure 13) shows a completely *syn* arrangement of $\text{P}=\text{C}$ and $\text{C}=\text{O}$

As expected from the favourable values of $^2J_{\text{P-CO}}$ and previous work in the area, the fluorinated ylides **38–45** underwent clean loss of Ph_3PO upon FVP to give alkynes **46–53**, respectively (Figure 14, Table 3). The transformation of **40** into **48**, **41** into **49**, and **43** into **51** have already been reported while the remaining reactions furnished the previously unreported fluorinated alkynes **46**, **47**, **50**, **52**, and **53** in good yield.

Cm pd	Yield (%)	^{31}P (δ)	NMR	FVP Temp	Prod uct	Yield (%)	Ref
38	77	+19.4		750 °C	46	81	^a
39	64	+17.7		750 °C	47	76	^a
40	76	+19.6			48	94	⁵⁶
41	60	+17.7			49	95	⁵⁷
42	89	+20.2		750 °C	50	96	^a
43	53	+19.6			51	80.5	⁵⁹
44	53	+18.8		550 °C	52	77	^a
45	77	+18.6		550 °C	53	74	^a

^a This work

3. Conclusion

The value of the two-bond coupling constant between the carbonyl carbon and phosphorus is readily determined from the ^{13}C NMR spectra of carbonyl-stabilised phosphonium ylides. This parameter shows a strong correlation both with the *syn* vs. *anti* arrangement of the $\text{C}=\text{P}$ and $\text{C}=\text{O}$ functions as determined by X-ray diffraction, and with the likely success of thermal extrusion of Ph_3PO to give alkynes. Specifically extrusion is not possible for cases where $^2J_{\text{P-CO}}$ is greater than 11 Hz. The series of three cyclic ylides provide a good illustration with the 5-membered ring compound undergoing decomposition while the 6- and 7-membered rings provide a new route to generate cyclohexyne and cycloheptyne respectively, these being isolated after rearrangement as the corresponding cyclic 1,3-dienes. A range of new highly fluorinated ylides have also been prepared and the J values correctly predict their successful thermolysis to give new highly fluorinated alkynes.

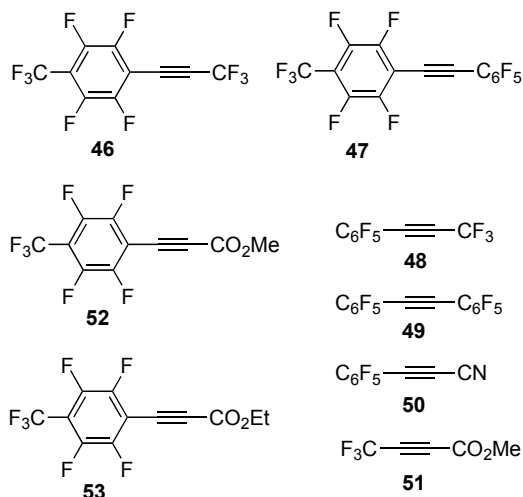


Figure 14. Fluorinated alkynes produced by ylide FVP

4. Experimental Section

4.1 General

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. NMR spectra were recorded for ^1H at 300 MHz, for ^{13}C at 75 MHz, for ^{19}F at 282 MHz and for ^{31}P at 121 MHz on a Bruker AM300 instrument. Spectra were obtained for solutions in CDCl_3 with Me_4Si as internal reference for ^1H and ^{13}C , CFCl_3 as external reference for ^{19}F and 85% H_3PO_4 as external reference for ^{31}P . CCDC 963473 (**25**), CCDC 963474 (**26**), CCDC 172040 (**27**), CCDC 963475 (**30**), CCDC 963476 (**31**), CCDC 963477 (**32**) and CCDC 963478 (**38**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2 Preparation of ylides for ^{13}C NMR and X-ray structure determination

4.2.1 Diethyl triphenylphosphoranylidene malonate (**24**)

This was prepared from diethyl bromomalonate and Ph_3P in the presence of Et_3N ,⁸⁷ as colourless crystals, mp 105–107 °C (Lit.,⁸⁷ 106–107 °C), ^{13}C NMR (CDCl_3 , 55 °C): δ =167.6 (d, J =13.1 Hz; CO), 131.9 (d, J =10 Hz; Ph, C-2), 131.6 (d, J =3 Hz; Ph, C-4), 128.2 (d, J =12 Hz; Ph, C-3), 127.0 (d, J =94 Hz; Ph, C-1), 58.2 (CH_2), 52.6 (d, J =121 Hz; C=P), 13.9 ppm (CH_3).

4.2.2 Acetylmethylenetriphenylphosphorane (**25**)

A colourless plate suitable for X-ray diffraction was obtained by recrystallisation from ethyl acetate. Data were recorded at 293(2) K on a Rigaku Mercury 70 diffractometer using $\text{Cu-K}\alpha$ radiation and the structure was solved by direct methods and refined using full-matrix least squares analysis. The following crystal data were obtained: $\text{C}_{21}\text{H}_{19}\text{OP}$, $M = 318.33$, colourless plate, monoclinic space group $P2(1)/n$; $a = 8.8756(10)$, $b = 19.405(2)$, $c = 10.4937(11)$ Å, $\beta = 94.394(2)^\circ$, $V = 1802.1(3)$ Å³, $Z = 4$, $D_c = 1.173$ g cm⁻³, $R = 0.0559$, $R_w = 0.1073$ for 1250 data with $I > 2\sigma(I)$ and 209 parameters.

4.2.3 1-(Methyl(2-methylphenyl)phenylphosphoranylidene)-3,3-dimethylbutan-2-one (**26**)

This was prepared as previously described.⁴⁴ A colourless platelet suitable for X-ray diffraction was obtained by recrystallisation from EtOAc . Data were recorded at 293(2) K on a Rigaku Mercury 70 diffractometer using $\text{Mo-K}\alpha$ radiation and the structure was solved by direct methods and refined using full-

matrix least squares analysis. The following crystal data were obtained: $\text{C}_{20}\text{H}_{25}\text{OP}$, $M = 312.37$, monoclinic space group $P2_1/c$; $a = 9.905(2)$, $b = 23.109(5)$, $c = 15.149(3)$ Å, $\beta = 90.460(6)^\circ$, $V = 3467.6(12)$ Å³, $Z = 8$, $D_c = 1.197$ g cm⁻³, $R = 0.073$, $R_w = 0.2075$ for 4939 data with $I > 2\sigma(I)$ and 397 parameters.

4.2.4 1,3-Diphenyl-2-triphenylphosphoranylidene propane-1,3-dione (**27**)

To a boiling solution of benzoylmethylenetriphenylphosphorane⁸⁸ **5** (10.0 g, 26 mmol) in toluene (150 mL) containing triethylamine (4.1 mL, 3.0 g, 30 mmol), a solution of benzoyl chloride (3.65 g, 26 mmol) in toluene (25 mL) was added dropwise over 1 h resulting in the formation of a white precipitate. After the addition, the mixture was heated under reflux for 3 h. The cooled solution was added to water (200 mL) and the resulting mixture extracted with CH_2Cl_2 (2×250 mL). The combined organic extracts were washed with water (2×100 mL), dried and evaporated to give a yellow oil which crystallised with time. Recrystallisation as described below from ethyl acetate gave the product **27** (8.9 g, 71%) as colourless crystals.

It should be noted that the yield obtained here is believed to be close to the maximum obtainable since evaporation of the filtrate at the end gave a thick yellow oil obviously containing by-products. In addition, although ethyl acetate gave excellent purity ylide in well-formed prisms, the solubility of the ylide in this solvent is low. For the optimum purification of the product we recommend that the crude product from a reaction on the scale mentioned above is heated to boiling with ethyl acetate (250 cm³). Once saturation has been achieved, the hot solution is decanted off through a fluted filter paper into a flask and allowed to cool. The resulting product is filtered off and the filtrate added back into the flask containing the crude product, together with any solid from the initial filtration, and once again brought to the boil. Only once this sequence had been repeated four times was complete dissolution of the product achieved. Evaporation of the final filtrate to half volume gave a small final crop of product. All crops obtained were of equal purity having mp 192–193 °C (lit.,⁴⁵ 191–192 °C); ^1H NMR: δ =7.70–7.80 (m, 6H), 7.40–7.50 (m, 13H), 6.90–7.00 ppm (m, 6H); ^{13}C NMR: δ =192.7 (d, J =7 Hz; CO), 142.7 (d, J =8 Hz; PhCO, C-1), 133.4 (d, J =9 Hz; PPh, C-2,6), 131.8 (d, J =2 Hz; PPh, C-4), 129.5 (PhCO, C-4), 128.8 (PhCO, C-2,6), 128.6 (d, J =13 Hz; PPh, C-3,5), 127.2 (PhCO, C-3,5), 126.2 (d, J =92 Hz; PPh, C-1), 83.1 ppm (d, J =102 Hz; P=C), ^{31}P NMR: δ =+19.6 ppm.

The product obtained was suitable for X-ray diffraction. Data were recorded at 293(2) K on a Bruker SMART diffractometer using $\text{Mo-K}\alpha$ radiation and the structures were solved by direct methods and refined using full-matrix least squares analysis. The following crystal data were obtained: $\text{C}_{33}\text{H}_{25}\text{O}_2\text{P}$, $M = 484.50$, colourless prism, monoclinic space group $P2_1/n$; $a = 15.3685(7)$, $b = 8.3421(8)$, $c = 19.9017(17)$ Å, $\beta = 98.438(5)^\circ$, $V = 2523.9(3)$ Å³, $Z = 4$, $D_c = 1.275$ g cm⁻³, $R = 0.0705$, $R_w = 0.1770$ for 2526 data with $I > 2\sigma(I)$ and 326 parameters.

4.2.5 Ethyl 3-triphenylphosphoranylidene pyruvate (**30**)

This was prepared using the published method⁵⁵ and recrystallised from toluene to give crystals suitable for X-ray diffraction. Data were recorded at 293(2) K on a Bruker SMART diffractometer using $\text{Mo-K}\alpha$ radiation and the structures were solved by direct methods and refined using full-matrix least squares analysis. The following crystal data were obtained: $\text{C}_{23}\text{H}_{21}\text{O}_3\text{P}$, $M = 376.37$, colourless prism, monoclinic space group $P2_1/n$; $a = 12.00380(10)$, $b = 9.02880(10)$, $c = 19.0573(3)$ Å, $\beta = 106.6540(10)^\circ$, $V = 1978.79(4)$ Å³, $Z = 4$, $D_c = 1.263$ g

cm^{-3} , $R = 0.0356$, $R_w = 0.0940$ for 2423 data with $I > 2\sigma(I)$ and 245 parameters.

4.2.6 1-(2-methoxyphenyl)-3-phenyl-3-triphenylphosphoranylidene-2-propane-1,2-dione (31)

This was prepared using the published method⁵⁸ as yellow crystals directly suitable for X-ray diffraction. Data were recorded at 93(2) K on a Rigaku Mercury 70 diffractometer using Mo-K α radiation and the structures were solved by direct methods and refined using full-matrix least squares analysis. The following crystal data were obtained: $\text{C}_{34}\text{H}_{27}\text{O}_3\text{P}$, $M = 514.53$, triclinic space group $P\bar{1}$; $a = 9.828(2)$, $b = 10.622(3)$, $c = 13.692(2)$ Å, $\alpha = 74.94(2)$, $\beta = 73.96(2)$, $\gamma = 78.45(2)^\circ$, $V = 1313.7(5)$ Å³, $Z = 2$, $D_c = 1.301$ g cm⁻³, $R = 0.0579$, $R_w = 0.1550$ for 2874 data with $I > 2\sigma(I)$ and 343 parameters.

4.2.7 Methyl 2,4-dioxo-3-triphenylphosphoranylidene-pentanoate (32)

This was prepared as previously described.²¹ A purple prism suitable for X-ray diffraction was obtained by recrystallisation from ethyl acetate. Data were recorded at 293(2) K on a Bruker SMART diffractometer using Mo-K α radiation and the structure was solved by direct methods and refined using full-matrix least squares analysis. The following crystal data were obtained: $\text{C}_{24}\text{H}_{21}\text{O}_4\text{P}$, $M = 404.38$, monoclinic space group $P2_1/c$; $a = 12.7684(5)$, $b = 9.1236(3)$, $c = 17.6495(6)$ Å, $\beta = 92.291(1)^\circ$, $V = 2054.41(13)$ Å³, $Z = 4$, $D_c = 1.307$ g cm⁻³, $R = 0.032$, $R_w = 0.079$ for 2454 data with $I > 2\sigma(I)$ and 263 parameters.

4.3 Representative ¹³C NMR data for ylides in Table 2

1 ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$)⁵¹ $\delta = 178.5$ (d, $J = 26$ Hz; CO), 133.1 (d, $J = 10$ Hz; Ph C-2), 132.3 (d, $J = 2$ Hz; Ph C-4), 128.5 (d, $J = 12$ Hz; Ph C-3), 123.8 (d, $J = 88$ Hz; Ph C-1), 62.2 (d, $J = 110$ Hz; P=C), 10.2 ppm (d, $J = 11$ Hz; CH₃).

1 ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Bu}^t$)⁷¹ $\delta = 199.9$ (s, CO), 132.7 (d, $J = 10$ Hz; Ph C-2), 131.4 (d, $J = 2$ Hz; Ph C-4), 128.4 (d, $J = 12$ Hz; Ph C-3), 127.6 (d, $J = 91$ Hz; Ph C-1), 47.0 (d, $J = 110$ Hz; P=C), 40.3 (d, $J = 12$ Hz; C), 28.6 ppm (3 CH₃).

1 ($\text{R}^1 = \text{Pr}$, $\text{R}^2 = \text{Bu}^t$)⁷¹ $\delta = 193.4$ (s, CO), 132.9 (d, $J = 9$ Hz; Ph C-2), 130.4 (d, $J = 2$ Hz; Ph C-4), 128.0 (d, $J = 12$ Hz; Ph C-3), 129.8 (d, $J = 96$ Hz; Ph C-1), 68.2 (d, $J = 105$ Hz; P=C), 39.8 (d, $J = 11$ Hz; C), 29.1 (d, $J = 12$ Hz; CH₂), 28.6 (3 CH₃), 28.2 (CH₂), 13.6 ppm (CH₃).

1 ($\text{R}^1 = \text{Pr}$, $\text{R}^2 = \text{c-Hex}$)⁷¹ $\delta = 193.5$ (s, CO), 133.2 (d, $J = 9$ Hz; Ph C-2), 130.9 (d, $J = 1$ Hz; Ph C-4), 128.1 (d, $J = 12$ Hz; Ph C-3), 128.3 (d, $J = 90$ Hz; Ph C-1), 63.9 (d, $J = 103$ Hz; P=C), 43.3 (d, $J = 10$ Hz; CH), 29.9 (2 CH₂), 29.0 (d, $J = 14$ Hz; CH₂), 28.1 (CH₂), 26.4 (2 CH₂), 26.1 (CH₂), 13.6 ppm (CH₃).

1 ($\text{R}^1 = \text{Pr}^i$, $\text{R}^2 = 2\text{-MeOC}_6\text{H}_4$)⁷⁴ $\delta = 184.5$ (d, $J = 5.3$ Hz; CO), 156.0 (Ar C-2), 134.1 (d, $J = 13$ Hz; Ar C-1), 133.6 (d, $J = 10$ Hz; Ph C-2), 131.0 (d, $J = 3$ Hz; Ph C-4), 128.3 (d, $J = 12$ Hz; Ph C-3), 128.3 (Ar CH), 128.2 (d, $J = 90$ Hz; Ph C-1), 127.9 (Ar CH), 120.0 (Ar CH), 110.7 (Ar CH), 75.5 (d, $J = 98$ Hz; P=C), 55.6 (OMe), 27.5 (d, $J = 13$ Hz; CHMe₂), 24.7 ppm (br; CHMe₂).

1 ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = 2\text{-MeO-5-ClC}_6\text{H}_3$) mp 212–214 °C; ¹H NMR: $\delta = 7.80\text{--}7.30$ (m, 15H; PPh), 7.18 (d, $J = 8$ Hz, 1H; Ar), 6.78 (s, 5H; CPh), 6.70–6.55 (m, 2H; Ar), 3.62 ppm (s, 3H; OMe); ¹³C NMR: $\delta = 184.0$ (d, $J = 6.7$ Hz; CO), 156.5 (Ar C-2), 137.4 (d, $J = 12$ Hz; Ar C-1), 133.9 (d, $J = 5$; Ph C-2); 133.6 (d,

$J = 10$ Hz; PPh C-2), 133.2 (Ar C-5), 131.8 (d, $J = 12$ Hz; Ph C-1), 131.4 (d, $J = 3$ Hz; PPh C-4), 129.9 (Ph C-4), 128.4 (d, $J = 12$ Hz; PPh C-3), 126.7 (d, $J = 2$ Hz; Ph C-3), 126.6 (d, $J = 91$ Hz; PPh C-1), 124.3 (d, $J = 2$ Hz; Ar C-6), 119.8 (Ar C-4), 111.1 (Ar C-3), 74.0 (d, $J = 107$ Hz; P=C), 55.4 ppm (OMe); ³¹P NMR: $\delta = +15.2$ ppm; elemental analysis calcd (%) for $\text{C}_{33}\text{H}_{26}\text{ClO}_2\text{P}$: C 76.07, H 5.03; found: C 76.02, H 4.96.

1 ($\text{R}^1 = 2\text{-MeOC}_6\text{H}_4$, $\text{R}^2 = 2\text{-MeSC}_6\text{H}_4$)⁶⁶ $\delta = 185.6$ (d, $J = 6.1$ Hz; CO), 157.9 (d, $J = 3$ Hz; C-OMe), 142.9 (d, $J = 12$ Hz; Ar C-1), 136.5 (d, $J = 6$ Hz), 136.4 (C-SMe), 133.6 (d, $J = 10$ Hz; Ph C-2), 131.1 (d, $J = 3$ Hz; Ph C-4), 128.0 (d, $J = 12$ Hz; Ph C-3), 127.8 (Ar CH), 127.3 (Ar CH), 127.2 (d, $J = 2$ Hz; Ar CH), 126.9 (d, $J = 91$ Hz; Ph C-1), 126.9 (d, $J = 10$ Hz; Ar C-1), 126.1 (Ar CH), 123.7 (Ar CH), 119.9 (d, $J = 1$ Hz; Ar CH), 109.2 (d, $J = 2$ Hz; Ar CH), 67.8 (d, $J = 109$ Hz; P=C), 54.0 (OMe), 17.0 ppm (SMe).

4.4 Preparation of cyclic ylides

Preparation of ylides **35–37** was carried out in four steps following the reported procedure.⁸² The appropriate ω -bromocarboxylic acid (0.1 mol) was converted to the ethyl ester by boiling in ethanol (100 cm³) in the presence of H₂SO₄ (0.1 cm³) for 3 h. The solution was evaporated and the residue dissolved directly in A.R. acetone (50 cm³). To this was added a solution of sodium iodide (18.0 g, 0.12 mol) in A.R. acetone (50 cm³). After stirring at RT for 12 h the mixture was evaporated and the residue partitioned between toluene (100 cm³) and water. The toluene layer containing the iodoester was dried and triphenylphosphine (26.2 g, 0.1 mol) added. This solution was heated under reflux for 12 h and, after cooling, the supernatant liquid was decanted off from the lower oily layer of the phosphonium salt which was washed twice with toluene by decantation. The salt was then dissolved in *t*-butanol (150 cm³), potassium *t*-butoxide (11.0 g, 97 mmol) was added and the solution heated under reflux for 12 h. The resulting mixture was evaporated and the residue partitioned between CH₂Cl₂ and water. Drying and evaporation of the organic phase gave the desired ylide, which was recrystallised from ethyl acetate.

4.4.1 2-Triphenylphosphoranylidene-cyclopentanone (35)

Colourless crystals (25%), m.p. 221–223 °C (lit.⁸⁹ 229–233 °C); ¹H NMR: $\delta = 7.8\text{--}7.3$ (m, 15H), 2.6–1.9 ppm (m, 6H); ¹³C NMR: $\delta = 196.1$ (d, $J = 11.3$ Hz; CO), 133.6 (d, $J = 10$; Ph C-2), 132.2 (d, $J = 3$ Hz; Ph C-4), 128.9 (d, $J = 12$ Hz; Ph C-3), 126.0 (d, $J = 90$ Hz; Ph C-1), 56.3 (d, $J = 107$ Hz; P=C), 40.1 (d, $J = 16$ Hz; C-5), 31.5 (d, $J = 14$ Hz; C-4), 23.7 ppm (d, $J = 14$ Hz; C-3); ³¹P NMR: $\delta = +12.6$ ppm.

4.4.2 2-Triphenylphosphoranylidene-cyclohexanone (36)

Colourless crystals (38%), m.p. 248–250 °C (lit.⁸² 245–247 °C); ¹H NMR: $\delta = 7.8\text{--}7.3$ (m, 15H), 2.25 (m, 2H), 2.0–1.6 ppm (m, 6H); ¹³C NMR: $\delta = 187.7$ (d, $J = 3.7$ Hz; CO), 133.2 (d, $J = 10$; Ph C-2), 131.1 (d, $J = 2$ Hz; Ph C-4), 128.1 (d, $J = 12$ Hz; Ph C-3), 126.7 (d, $J = 89$ Hz; Ph C-1), 58.9 (d, $J = 101$ Hz; P=C), 36.2 (d, $J = 10$ Hz; C-6), 26.4 (d, $J = 11$ Hz; C-3/4), 25.1 (d, $J = 11$ Hz; C-3/4), 23.9 ppm (C-5); ³¹P NMR: $\delta = +17.4$ ppm.

4.4.3 2-Triphenylphosphoranylidene-cycloheptanone (37)

Colourless crystals (20%), m.p. 205–206 °C (lit.⁸² 205–208 °C); ¹H NMR: $\delta = 7.8\text{--}7.3$ (m, 15H), 2.7–2.4 (m, 2H), 2.0–1.3 ppm (m, 8H); ¹³C NMR: $\delta = 195.3$ (d, $J = 4.2$ Hz; CO), 133.4 (d, $J = 10$; Ph C-2), 131.3 (d, $J = 2$ Hz; Ph C-4), 128.5 (d, $J = 12$ Hz; Ph C-3), 127.7 (d, $J = 90$ Hz; Ph C-1), 63.6 (d, $J = 105$ Hz; P=C), 42.9 (d, $J = 12$ Hz; C-7), 32.6 (C-5/6), 32.4 (d, $J = 4$ Hz; C4), 26.9 (d, $J = 13$ Hz; C-3), 25.5 ppm (C-5/6); ³¹P NMR: $\delta = +17.6$ ppm.

4.4.4 FVP of Cyclic Ylides

This was carried out in a conventional flow system by subliming the starting material (100–200 mg) through a horizontal quartz tube (30 × 2.5 cm) externally heated by a tube furnace at temperatures in the range 500–800 °C and maintained at a pressure of $2\text{--}3 \times 10^{-2}$ torr by a rotary vacuum pump. Products were collected in a liquid N₂ cooled U-shaped trap and identified as noted. Yields were determined by adding an accurately weighed quantity of CH₂Cl₂ and comparing ¹H NMR integrals.

FVP of **35** led to recovery of unchanged starting material up to 850 °C, while at 900 °C there was extensive decomposition to give only low yields of Ph₃P; ³¹P NMR: $\delta = -5.0$ ppm, and benzene; ¹H NMR: $\delta = 7.36$ ppm (s).

FVP of **36** up to 650 °C led to recovery of unchanged starting material. At 750 °C there was complete reaction to give, at the furnace exit, Ph₃PO (75%); ³¹P NMR: $\delta = +29.2$ ppm, and in the cold trap, cyclohexa-1,3-diene (34%); ¹H NMR: $\delta = 5.9\text{--}5.8$ (m, 4H), 2.15 (m, 4H) ppm, and benzene (34%); ¹H NMR: $\delta = 7.36$ ppm (s).

FVP of **37** up to 650 °C led to recovery of unchanged starting material. At 750 °C there was complete reaction to give, at the furnace exit, Ph₃PO (80%); ³¹P NMR: $\delta = +29.2$ ppm, and in the cold trap, cyclohepta-1,3-diene (75%); ¹H NMR: $\delta = 5.72$ (m, 4H), 2.32 (m, 4H), 1.9–1.7 (m, 2H) ppm.

4.5 Preparation of Fluorinated Ylides

Ylides **38**, **39**, **40**, **41**, **44** and **45** were prepared using the method shown in Scheme 2 as follows. A suspension of methyltriphenylphosphonium bromide (12.0 g, 33.6 mmol) in dry THF (70 mL) was stirred under nitrogen while *n*-butyllithium in hexanes (2.5 M, 13.5 mL, 33.7 mmol) was added slowly at RT. After 20 min either hexafluorobenzene or octafluorotoluene (16.8 mmol) in dry THF (10 mL) was added and the mixture was stirred for 1 h after which time a deep red precipitate had formed. To this mixture a solution of pentafluorobenzoyl chloride, trifluoroacetic anhydride, or methyl or ethyl oxalyl chloride (8.4 mmol) in dry THF (5 mL) was added and the mixture was stirred overnight before being added to water. Extraction with diethyl ether (3 × 50 mL), drying and evaporation gave the products, which were recrystallised from ethyl acetate.

Ylide **42** was prepared by slowly adding triethylamine (3.0 g, 29.6 mmol) to a suspension of cyanomethyltriphenylphosphonium chloride⁹⁰ (5.0 g, 14.8 mmol) in THF (60 mL) stirred at 0 °C. After 20 min, pentafluorobenzoyl chloride (3.41 g, 14.8 mmol) was added dropwise and the resulting mixture was allowed to warm to RT and stirred for 24 h. It was the added to water and the resulting solid was filtered off, washed with water and dried. Recrystallisation from ethyl acetate gave the pure product.

Ylide **43** was prepared by the literature method.⁵⁹

4.5.1 [(2,3,5,6-Tetrafluoro-4-trifluoromethylphenyl)(trifluoroacetyl)methylene]triphenylphosphorane (**38**)

Pale yellow crystals (77%) from ethyl acetate, mp 190–191 °C; ¹H NMR: $\delta = 7.70\text{--}7.56$ (br m, 9H), 7.53–7.43 ppm (br m, 6H); ¹³C NMR: $\delta = 171.1$ (q of d, $J_{\text{CF}} = 32$ Hz, $J_{\text{CP}} = 7.0$ Hz; CO), 147.1 (d of m, $J = 242$ Hz; 2CF), 143.3 (d of m, $J = 258$ Hz; 2CF), 133.4 (d, $J = 10$ Hz; Ph, C-2), 133.1 (d, $J = 3$ Hz; Ph, C-4), 129.1 (d, $J = 13$ Hz; Ph, C-3), 122.6 (d, $J = 92$ Hz; Ph, C-1), 120.6 (q of m, $J = 273$ Hz; ArCF₃), 120.3 (m; C), 118.3 (q of d, $J_{\text{CF}} = 289$ Hz, $J_{\text{CP}} = 17$ Hz; COCF₃), 53.7 ppm (d, $J = 117$ Hz; P=C); ¹⁹F NMR: $\delta =$

–56.9 (t, $J = 21$ Hz, 3F; ArCF₃), –72.5 (s, 3F; COCF₃), –133.9 (m, 2F), –143.2 ppm (m, 2F); ³¹P NMR: $\delta = +19.4$ ppm; HRMS (ES⁺): m/z calcd for C₂₈H₁₆F₁₀OP: 589.0779 [$M+H^+$]; found: 589.0759.

Crystals suitable for X-ray diffraction were obtained by slow evaporation of the NMR solution. Data were recorded at 93(2) K on a Rigaku Mercury 70 diffractometer using Mo-K α radiation and the structures were solved by direct methods and refined using full-matrix least squares analysis. The following crystal data were obtained: C₂₈H₁₅F₁₀OP•CDCl₃, $M = 707.76$, colourless prism, monoclinic space group $P2_1/c$; $a = 9.8234(14)$, $b = 18.318(3)$, $c = 16.330(3)$ Å, $\beta = 97.022(7)^\circ$, $V = 2916.5(7)$ Å³, $Z = 4$, $D_c = 1.612$ g cm^{–3}, $R = 0.0529$, $R_w = 0.1498$ for 3634 data with with $I > 2\sigma(I)$ and 397 parameters.

4.5.2 [(Pentafluorobenzoyl)(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)methylene]triphenylphosphorane (**39**)

Pale orange crystals (64%) from ethyl acetate, mp 156–158 °C; ¹H NMR: $\delta = 7.92\text{--}7.58$ (m, 9H), 7.55–7.45 ppm (m, 6H); ¹³C NMR: $\delta = 173.4$ (d, $J = 6.6$ Hz), 146.5 (d of m, $J = 241$ Hz; 2CF), 143.3 (d of m, $J = 247$ Hz; 2CF), 140.8 (d of m, $J = 238$ Hz; CF), 137.1 (d of m, $J = 252$ Hz; 2CF), 133.5 (d, $J = 10$ Hz; Ph, C-2), 132.9 (d, $J = 3$ Hz; Ph, C-4), 129.0 (d, $J = 13$ Hz; Ph, C-3), 123.4 (d, $J = 92$ Hz; Ph, C-1), 121.9 (m, C), 119.3 (m, C), 59.6 ppm (d, $J = 117$ Hz; P=C); ¹⁹F NMR: $\delta = -56.8$ (t, $J = 22$ Hz, 3F; CF₃), –134.7 (m, 2F), –142.6 (m, 4F), –155.1 (t, $J = 21$ Hz, 1F), –161.9 ppm (m, 2F); ³¹P NMR: $\delta = +17.7$ ppm; MS (CI⁺): m/z 686.09 [$M+H^+$].

4.5.3

[(Pentafluorophenyl)(trifluoroacetyl)methylene]triphenylphosphorane (**40**)

Colourless crystals (76%) from ethyl acetate, mp 208–210 °C (Lit.,⁵⁶ 209–210 °C); ¹H NMR: $\delta = 7.70\text{--}7.55$ (br m, 9H), 7.52–7.43 ppm (br m, 6H); ¹³C NMR: $\delta = 171.6$ (q of d, $J_{\text{CF}} = 31$ Hz, $J_{\text{CP}} = 8.2$ Hz; CO), 147.1 (d of m, $J = 241$ Hz; 2CF), 140.6 (d of m, $J = 252$ Hz; CF), 136.8 (d of m, $J = 250$ Hz; 2CF), 133.4 (d, $J = 10$; Ph, C-2), 132.9 (d, $J = 3$ Hz; Ph, C-4), 128.9 (d, $J = 12$ Hz; Ph, C-3), 123.0 (d, $J = 92$ Hz; Ph, C-1), 118.4 (q of d, $J_{\text{CF}} = 289$ Hz, $J_{\text{CP}} = 17$ Hz; CF₃), 53.3 ppm (d, $J = 117$ Hz; P=C); ¹⁹F NMR: $\delta = -72.4$ (s, 3F; COCF₃), –135.7 (m, 2F), –154.9 (t, $J = 21$ Hz, 1F), –164.4 ppm (m, 2F); ³¹P NMR: $\delta = +19.6$ ppm.

4.5.4

[(Pentafluorobenzoyl)(pentafluorophenyl)methylene]triphenylphosphorane (**41**)

Colourless crystals (60%) from ethyl acetate, mp 255–256 °C (Lit.,⁵⁷ 245–246 °C); ¹H NMR: $\delta = 7.73$ (m, 6H), 7.58 (m, 3H), 7.48 ppm (m, 6H); ¹³C NMR: $\delta = 173.6$ (d, $J = 8.0$ Hz; CO), 146.7 (d of m, $J = 240$ Hz; 2CF), 143.1 (d of m, $J = 246$ Hz; 2CF), 140.6 (d of m, $J = 252$ Hz; CF), 140.1 (d of m, $J = 255$ Hz; CF), 137.0 (d of m, $J = 252$ Hz, 2CF), 136.8 (d of m, $J = 251$ Hz; 2CF), 133.5 (d, $J = 10$ Hz; Ph, C-2), 132.7 (d, $J = 3$ Hz; Ph, C-4), 128.9 (d, $J = 13$ Hz; Ph, C-3), 123.6 (d, $J = 90$ Hz; Ph, C-1), 117.1 (m; C), 111.7 (m; C), 58.6 ppm (d, $J = 115$ Hz; P=C); ¹⁹F NMR: $\delta = -136.2$ (m, 2F), –142.5 (m, 2F), –155.3 (m, 1F), –155.7 (t, $J = 21$ Hz, 1F), –162.2 (m, 2F), –163.6 ppm (m, 2F); ³¹P NMR: $\delta = +17.7$ ppm.

4.5.5

[(Cyano)(pentafluorobenzoyl)methylene]triphenylphosphorane (**42**)

Colourless crystals (89%) from ethyl acetate, mp 222–224 °C; ¹H NMR: $\delta = 7.74\text{--}7.65$ (9H, m), 7.62–7.54 ppm (6H, m); ¹³C NMR: $\delta = 178.7$ (d, $J = 5.8$ Hz; CO), 143.2 (d of m, $J = 247$ Hz; 2CF), 141.5 (d of m, $J = 253$ Hz; CF), 137.4 (d of m, $J = 252$ Hz;

2CF), 133.7 (d, $J=2$ Hz; Ph, C-4), 133.6 (d, $J=10$ Hz; Ph, C-2), 129.4 (d, $J=13$ Hz; Ph, C-3), 121.6 (d, $J=93$ Hz; Ph, C-1), 120.0 (d, $J=15$ Hz; CN), 54.6 ppm (d, $J=122$ Hz; C=P); ^{19}F NMR: $\delta = -142.7$ (m, 2F), -154.2 (t, $J=21$ Hz, 1F), -161.6 ppm (m, 2F); ^{31}P NMR: $\delta = +20.2$ ppm; HRMS (CI^+): m/z calcd for $\text{C}_{27}\text{H}_{16}\text{F}_5\text{NOP}$: 496.0890 [$M+\text{H}^+$]; found: 496.0881.

4.5.6 Methyl 4,4,4-Trifluoro-3-oxo-2-(triphenylphosphoranylidene)butanoate (43)

Colourless crystals (53%) from ethyl acetate, mp 118–120 °C (Lit.⁵⁹ 118–120 °C); ^1H NMR: $\delta = 7.70$ – 7.63 (m, 6H), 7.61 – 7.55 (m, 3H), 7.51 – 7.46 (m, 6H), 3.29 ppm (s, 3H; OMe) (agreement with Lit.⁵⁹); ^{13}C NMR: $\delta = 174.8$ (q of d, $J_{\text{CF}}=34$ Hz, $J_{\text{CP}}=6.1$ Hz; COCF_3), 166.0 (d, $J=13$ Hz; CO_2Me), 133.2 (d, $J=10$; Ph, C-2), 132.5 (d, $J=3$ Hz; Ph, C-4), 128.8 (d, $J=13$ Hz; Ph, C-3), 123.8 (d, $J=93$ Hz; Ph, C-1), 117.9 (q of d, $J_{\text{CF}}=288$ Hz, $J_{\text{CP}}=14.5$ Hz; CF_3), 70.0 (d, $J=111$ Hz; P=C), 50.7 ppm (OMe); ^{19}F NMR: $\delta = -72.1$ ppm (s; COCF_3); ^{31}P NMR: $\delta = +19.6$ ppm.

4.5.7 Methyl 3-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-3-triphenylphosphoranylidene-2-oxopropanoate (44)

Colourless crystals (2.48 g, 53%), mp 192–198 °C; ^1H NMR: $\delta = 7.80$ – 7.40 (br m, 15H), 3.67 ppm (s, 3H; CH_3); ^{13}C NMR: $\delta = 172.7$ (d, $J=6.8$ Hz; CO), 164.4 (d, $J=15$ Hz; CO_2Me), 146.1 (d of m, $J=253$ Hz; 2CF), 143.2 (d of m, $J=259$ Hz; 2CF), 133.3 (d, $J=10$ Hz; Ph C-2), 132.6 (d, $J=3$ Hz; Ph C-4), 128.8 (d, $J=13$ Hz; Ph C-3), 122.9 (d, $J=92$ Hz; Ph C-1), 122.5 (m; $\text{C}_6\text{F}_4\text{CF}_3$, C-1), 120.7 (q of m, $J=275$ Hz; CF_3), 107.3 (m; $\text{C}_6\text{F}_4\text{CF}_3$ C-4), 57.9 (d, $J=116$ Hz; C=P), 51.9 ppm (CH_3); ^{19}F NMR: $\delta = -56.2$ (t, $J=22$ Hz, 3F; CF_3), -135.0 (m, 2F), -143.4 ppm (m, 2F); ^{31}P NMR: $\delta = +18.8$ ppm; HRMS (CI^+): m/z calcd for $\text{C}_{29}\text{H}_{19}\text{F}_7\text{O}_3\text{P}$: 579.0960 [$M+\text{H}^+$]; found: 579.0967.

4.5.8 Ethyl 3-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-3-triphenylphosphoranylidene-2-oxopropanoate (45)

Colourless crystals (3.83 g, 77%), mp 149–150 °C; ^1H NMR: $\delta = 7.80$ – 7.52 (m, 9H), 7.52 – 7.40 (m, 6H), 4.13 (q, $J=7$ Hz, 2H; CH_2), 1.21 ppm (t, $J=7$ Hz, 3H; CH_3); ^{13}C NMR: $\delta = 173.6$ (d, $J=6.6$ Hz; CO), 164.2 (d, $J=16$ Hz; CO_2Et), 146.2 (d of m, $J=248$ Hz; 2CF), 143.3 (d of m, $J=259$ Hz; 2CF), 133.4 (d, $J=10$ Hz; Ph C-2), 132.7 (d, $J=3$ Hz; Ph C-4), 128.9 (d, $J=13$ Hz; Ph C-3), 123.2 (d, $J=92$ Hz; Ph C-1), 123.0 (m; $\text{C}_6\text{F}_4\text{CF}_3$ C-1), 120.8 (q of m, $J=271$ Hz; CF_3), 107.3 (m; $\text{C}_6\text{F}_4\text{CF}_3$ C-4), 61.1 (CH_2), 57.4 (d, $J=117$ Hz; P=C), 13.8 ppm (CH_3); ^{19}F NMR: $\delta = -56.2$ (t, $J=22$ Hz, 3F; CF_3), -134.9 (m, 2 F) -143.5 ppm (m, 2 F); ^{31}P NMR: $\delta = +18.6$ ppm; HRMS (CI^+): m/z calcd for $\text{C}_{30}\text{H}_{21}\text{F}_7\text{O}_3\text{P}$: 593.1117 [$M+\text{H}^+$]; found: 593.1117.

4.6 FVP of Fluorinated Ylides

This was carried out, using the same set-up as described for the cyclic ylides, on a 10–25 mmol scale and with the furnace temperatures as shown in Table 3. After the pyrolysis, the alkynes were separated from Ph_3PO and obtained in pure form by trap-to-trap distillation (46) or column chromatography (SiO_2 , hexane) (47, 50, 52 and 53).

4.6.1 1-(2,3,5,6-Tetrafluoro-4-trifluoromethylphenyl)-3,3,3-trifluoroprop-1-yne (46)

Colourless liquid (3.34 g, 81%); ^{13}C NMR: $\delta = 147.7$ (d of m, $J=256$ Hz; 2CF), 144.1 (d of m, $J=261$ Hz; 2CF), 120.2 (q, $J=274$ Hz; ArCF_3), 113.8 (q, $J=258$ Hz; CF_3), 88.5 (q of m, $J=54$ Hz; $-\text{C}\equiv$), 70.3 ppm (m; $-\text{C}\equiv$); ^{19}F NMR: $\delta = -52.2$ (s, 3F), -57.2 (t, $J=22$ Hz, 3F), -132.2 (m, 2F), -139.1 ppm (m, 2F); HRMS (CI^+): m/z calcd for C_{10}F_9 : 290.9856 [$M-\text{F}^+$]; found: 290.9885.

4.6.2 Pentafluorophenyl(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)ethyne (47)

Colourless crystals, (1.91 g, 76%) m.p. 85–86 °C; ^{13}C NMR: $\delta = 147.4$ (d of m, $J=255$ Hz; 2CF), 147.0 (d of m, $J=261$ Hz; 2CF), 144.2 (d of m, $J=260$ Hz; 2CF), 143.0 (d of m, $J=259$ Hz; CF), 137.8 (d of m, $J=256$ Hz; 2CF), 120.6 (q, $J=272$ Hz; CF_3), 111.0 (q of t, $J=35$, 13 Hz) 107.3 (t, $J=17$ Hz), 98.3 (t, $J=18$ Hz), 87.6 (q, $J=4$ Hz, $-\text{C}\equiv$), 84.5 ppm (q, $J=3$ Hz; $-\text{C}\equiv$); ^{19}F NMR: $\delta = -57.1$ (t, $J=22$ Hz, 3F), -133.7 (m, 2F), -134.6 (m, 2F), -140.4 (m, 2F), -149.0 (t, $J=20$ Hz, 1F), -161.1 ppm (m, 2F); HRMS (CI^+): m/z calcd for $\text{C}_{15}\text{HF}_{12}$: 408.9887 [$M+\text{H}^+$]; found: 408.9892.

4.6.3 (Pentafluorophenyl)propynenitrile (50)

Colourless crystals, (5.21 g, 96%) m.p. 24–25 °C; ^{13}C NMR: $\delta = 149.1$ (d of m, $J=258$ Hz; 2CF), 144.4 (d of m, $J=262$ Hz; CF), 137.8 (d of m, $J=252$ Hz; 2CF), 104.0 (CN), 95.6 (t of d, $J=17$, 4 Hz; Ph, C-1), 73.0 (q, $J=3.5$ Hz; $-\text{C}\equiv$), 67.0 ppm (q, $J=4$ Hz; $-\text{C}\equiv$); ^{19}F NMR: $\delta = -132.2$ (m, 2F), -144.3 (t of t, $J=21$, 5 Hz, 1F), -159.2 ppm (m, 2F); HRMS (CI^+): m/z calcd for $\text{C}_9\text{HF}_5\text{N}$: 218.0029 [$M+\text{H}^+$]; found: 218.0027.

4.6.4 Methyl 3-(2,3,5,6-Tetrafluoro-4-trifluoromethylphenyl)propynoate (52)

Clear brown oil (3.00 g, 77%); ^1H NMR: $\delta = 3.90$ ppm (s; CH_3); ^{13}C NMR: $\delta = 152.6$ (CO), 147.8 (d of m, $J=257$ Hz, 2CF), 144.1 (d of m, $J=261$ Hz; 2CF), 120.4 (q, $J=275$ Hz; CF_3), 112.1 (qt, $J=35$, 13 Hz; Ar C-4), 105.6 (t, $J=17$ Hz; Ar C-1), 92.8 (t, $J=4$ Hz; $\equiv\text{C}-$), 68.8 (t, $J=4$ Hz; $\equiv\text{C}-$), 53.4 ppm (CH_3); ^{19}F NMR: $\delta = -56.6$ (t, $J=22$ Hz, 3F; CF_3), -131.9 (m, 2F), -139.2 ppm (m, 2F); HRMS (CI^+): m/z calcd for $\text{C}_{11}\text{H}_4\text{O}_2\text{F}_7$: 301.0100 [$M+\text{H}^+$]; found: 301.0095.

4.6.5 Ethyl 3-(2,3,5,6-Tetrafluoro-4-trifluoromethylphenyl)propynoate (53)

Clear brown oil (3.15 g, 74%); ^1H NMR: $\delta = 4.36$ (q, $J=7$ Hz, 2H; CH_2), 1.39 ppm (t, $J=7$ Hz, 3H; CH_3); ^{13}C NMR: $\delta = 152.2$ (CO), 147.8 (d of m, $J=255$ Hz; 2CF), 144.1 (d of m, $J=260$ Hz; 2CF), 120.4 (q, $J=274$ Hz; CF_3), 112.0 (qt, $J=35$, 13 Hz; Ar C-4), 105.7 (t, $J=17$ Hz; Ar C-1), 93.2 (t, $J=4$ Hz; $\equiv\text{C}-$), 68.3 (br, $\equiv\text{C}-$), 63.0 (CH_2), 13.8 ppm (CH_3); ^{19}F NMR: $\delta = -56.6$ (t, $J=22$ Hz, 3F; CF_3), -131.8 (m, 2F), -139.2 ppm (m, 2F); HRMS (CI^+): m/z calcd for $\text{C}_{12}\text{H}_6\text{O}_2\text{F}_7$: 315.0256 [$M+\text{H}^+$]; found: 315.0262.

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Supplementary Material

Copies of ^1H , ^{13}C , ^{19}F and ^{31}P NMR spectra.

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